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Nonlocality and optics of inhomogeneous systems: The role of quantum induction

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Nonlocal interactions play a prominent role in the optics of inhomogeneous systems. Classical discrete dipole descriptions take into account only electro-magnetic nonlocality. This is insufficient to describe correctly the inhomogeneous optical response (e.g., reflectance anisotropy) for covalently bonded systems like semiconductor surfaces. For those systems also a prominent quantum mechanical nonlocality exists. In a cellular description this can be understood easily from the behavior of the wave function. For strongly bonded systems the wave function extends across cell boundaries and when cells are polarized, neighboring cells get polarized as well. This quantum induction introduces nonlocal polarizabilities in the description. The technical details how discrete dipole models have to be adapted to use nonlocal polarizabilities in finite systems and crystalline slabs and surfaces are given in this paper. The modified method is called discrete cellular method.
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I. INTRODUCTION

Detection of surface chemical reactions can be achieved with monolayer and lower sensitivity using special optical techniques such as differential ellipsometry. Controlled use of this technique requires understanding of the behavior of light in the outermost monolayers of a surface. This represents a very important, but also very difficult theoretical problem and is a clear example of inhomogeneous optics. This paper will show how this class of problems can be dealt with using discrete methods. The consistent use of a discrete description for chemical or physical problems leaves out the treatment of space as a whole. Instead it requires a well-defined scheme for the subdivision of space. Familiar concepts like atoms or molecules are classical examples of such subdivision schemes. A subdivision needs a specification of the subvolumes or cells, and obviously, those cells have to be disjunct and should cover whole space. For diluted gases it is not necessary to know the cells in detail, but for fluids and solids we need to specify accurately how the cells are chosen. Concepts like atomic valence (or equivalently charge) are typical examples of cellular quantities in chemistry. For the static case these concepts have been treated thoroughly and in detail by Bader.[1] A cellular subdivision also underlies one of the classical models used in optics, the discrete dipole model. All concepts used in this model, polarizability, dipole strength or local field, are actually cellular quantities. Details about this description can be found in text books.[2]

The best known result of discrete dipole modeling is the familiar Lorentz–Lorenz expression, which relates the description based on polarizability of discrete dipoles and the continuum description based on the dielectric constant. However, this model presupposes a homogeneous isotropic bulk, where the short-range electromagnetic interactions cancel on symmetry grounds. For (strongly) inhomogeneous systems, such as surfaces, these short-range interactions are essential and become experimentally accessible. It is well known that classical discrete dipole models have poor performance for inhomogeneous systems, other than ionic solids, like alkali halogenides, or the weakly bonded solid argon.

The failure of the discrete dipole description for systems with stronger bonding, such as semiconductor surfaces, has to be ascribed primarily to the assumption that cells can be polarized independently from each other. This assumption is common in all discrete dipole descriptions, and those finite systems which obey this assumption, can be treated directly with it. Infinite systems like the (idealized) bulk or semi-infinite ones (which include the surfaces or interfaces in the description) cannot be treated easily. Those can only be handled if they are crystalline, allowing the use of translational symmetry. Discrete dipole descriptions for both bulk and surface systems of crystalline composition have been treated extensively in the literature.[3–8]

In classical discrete dipole theory the state of polarization of a cell depends only on the (local) electric field in the cell. This linear process is called induction, having as constant of proportionality the polarizability of the cell. In this paper we want to go beyond the assumption of independently polarizable cells. The only possible physical meaning of being dependent is that the polarization of a cell also influences the polarization of other cells. Why this occurs can be elucidated in a number of ways. The simplest and also most transparent way to make this influence clear is by looking at the behavior of the wave function. We pointed out that because of the discrete description itself, space has to be subdivided

in cells. Then in general the wave function will extend beyond the cell boundary and will exist in more than one cell only. Now if the state of polarization of a cell is going to change, this is only possible when the wave function inside that particular cell changes. If, however, the cell also has a boundary intersecting the wave function, the neighboring cell has to change its wave function too. This occurs, because the wave function has to be continuous and differentiable at the cell boundary. So the polarization of the neighboring cell has to change as well. We will call this extra (quantum mechanical) contribution to the state of polarization quantum induction. One can account for this quantum induction by making use of a nonlocal polarizability.

Although the possibility of a nonlocal polarizability can be made clear using very basic arguments, there are only few references in the literature[9] about its possible use within a discrete description. If the wave functions of the system are contained entirely within the cells, there is no quantum induction and the familiar description using local polarizabilities can be used. Then the system obeys a classical discrete dipole description. When these effects cannot be neglected, we will call the method discrete cellular. If we mention ''nonlocal'' in this paper without further details, we will mean nonlocal in the quantum induction sense.

The first successful results obtained by means of the discrete cellular method (DCM) have been for the anisotropic reflectance (RAS) frame GaAs (110) surfaces and have been published by us.[10] This paper contains both the general layout of the method and the results for the GaAs (110) case, including a comparison with experimental data. DCM consists of two separate parts: a modification of the discrete dipole method (DDM), such that it can handle nonlocal polarizabilities, and a quantum mechanical derivation of the nonlocal polarizabilities themselves. The present paper presents the detailed derivation of the first part, the adaptation of the discrete dipole method, the results of which have been outlined already in Ref. 10. The derivation of the nonlocal polarizabilities has been the subject of the thesis of one of the authors.[11]

The organization of the paper is as follows. In Sec. II we treat nonlocal induction, starting from a general continuum description. So polarization induces electric fields according to Eq. (6) and electric fields induce polarization according to Eq. (14). These continuum equations are discretized using a division of the total volume occupied by matter, V_0, into cells V_i. This discretization gives rise to the local field and cell polarizability, underlying DDM. The same discretization also gives rise to the average field and quantum mechanical nonlocal polarizability underlying DCM.

In Sec. III the induction mechanisms introduced in Sec. II are applied to finite systems represented by clusters of dipoles. Clusters build the easiest case and their scheme of solution is representative for the other cases.

Section IV has been included to show where the place is within the present nonlocal treatment of the generally used Lorentz–Lorenz relation.

Sections V and VI belong closely together since they treat infinite systems. Only infinite systems, obeying translational symmetry, can be treated rigorously. Parallel translational symmetry, as results for crystalline planes obeying Eq. (39), holds in both sections. With this kind of symmetry only, slabs can be treated already, since they consist of a finite number of planes.

Most of the complexity of the present paper goes to Sec. VI, where semi-infinite crystalline systems are treated. These systems have to obey the parallel translational symmetry of Sec. V, but employ in top of that also symmetry in a direction perpendicular to the planes. This bulk symmetry starts to become prominent only a relatively short distance below the surface and allows for a description of the bulk response by means of normal modes. The successful matching, including the full twofold nonlocality, of these normal modes to the outermost layer containing the surface itself, is the main achievement of this paper.

II. NONLOCAL INDUCTION

Under the conditions mentioned in the introduction, the basics of the discrete cellular method can be given. The treatment of the electromagnetic fields is exactly the same as for the discrete dipole method. It means that we exploit the continuity equations for charges and currents to replace both by a continuum polarization (density) field $\mathbf{P}$ and simultaneously we will use the Lorentz gauge to replace the scalar potential ϕ and vector potential $\mathbf{A}$ by the Hertz potential $\mathbf{Z}$.[12] The reduced set, containing only $(\mathbf{P},\mathbf{Z})$ as variables, obeys the dispersion equation:

$$\nabla^2\mathbf{Z}-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{Z}=-\frac{1}{\epsilon_0}\mathbf{P}. \tag{1}$$

For a harmonic driving field of frequency ω the solution of this equation is

$$\mathbf{Z}(\mathbf{r})=\frac{1}{4\pi\epsilon_0}\int d\mathbf{r}'\,\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}\mathbf{P}(\mathbf{r}'), \tag{2}$$

where $k=\omega/c$. From the Hertz potential all other fields and potentials can be derived. The vector potential $\mathbf{A}$ is the potential commonly used in existing quantum mechanical perturbation theories. This vector potential and the scalar potential Φ can be obtained from the Hertz potential by

$$\begin{aligned}\mathbf{A}&=\frac{1}{c^2}\frac{\partial\mathbf{Z}}{\partial t},\\ \mathbf{\Phi}&=-\nabla^T\mathbf{Z}.\end{aligned} \tag{3}$$

Here the upper T represents the transpose of a vector. When a transposed vector is followed by a second vector the notation implies the scalar product. If an upper T vector has been preceded by a second vector, the notation implies a direct product. The notation is particularly useful in discrete dipole theory, when applied to triple products of the kind ($\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ arbitrary vectors):

$$\mathbf{a}(\mathbf{b}^T\mathbf{c})=(\mathbf{a}\mathbf{b}^T)\mathbf{c}. \tag{4}$$

For optical frequencies the electric field **E** is the dominant field and the influence of magnetic fields **B** can be neglected. Hence it suffices to indicate how electric fields **E** have to be derived from the Hertz potential:

$$\mathbf{E}(r) = -\nabla\Phi(\mathbf{r}) - \frac{\partial \mathbf{A}(\mathbf{r})}{\partial t} = \nabla\nabla^T \mathbf{Z}(\mathbf{r}) - \frac{1}{c^2}\frac{\partial^2 \mathbf{Z}(\mathbf{r})}{\partial t^2}. \quad (5)$$

If we combine Eqs. (2) and (5) we find the general solution for the electric field, when an external field $\mathbf{B}_{\mathrm{Ext}}$ is applied to the system:

$$\begin{aligned} \mathbf{E}(\mathbf{r}) &= \mathbf{E}_{\mathrm{Ext}}(\mathbf{r}) + \int d\mathbf{r}'\, \overleftrightarrow{\mathbf{t}}(\mathbf{r}-\mathbf{r}')\mathbf{P}(\mathbf{r}'), \\ \overleftrightarrow{\mathbf{t}}(\mathbf{r}-\mathbf{r}') &= [\nabla\nabla^T + k^2 \overleftrightarrow{\mathbf{1}}] \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{4\pi\epsilon_0 |\mathbf{r}-\mathbf{r}'|}. \end{aligned} \quad (6)$$

Here $\overleftrightarrow{\mathbf{1}}$ is the unit tensor and $\overleftrightarrow{\mathbf{t}}$ the transfer kernel, describing the full nonlocal retarded electromagnetic interactions. (Note that in Ref. 10 we used the symbol **f** for the transfer kernel, but we want to reserve this symbol in this paper for the planar transfer tensor.) For $\mathbf{E}_{\mathrm{Ext}}$ we will use a plane wave:

$$\mathbf{E}_{\mathrm{Ext}}(\mathbf{r},t) = \mathbf{E}_0 e^{i[\mathbf{k}^T\mathbf{r} - \omega t]}. \quad (7)$$

Until here we have only used a continuum description. Discretization of the continuum equations yields the discrete dipole and discrete cellular descriptions. Discretization concerns primarily Eq. (6). When space is subdivided into N subvolumes V_i, we can apply the discrete dipole approximation to this equation:

$$\begin{aligned} \mathbf{E}(\mathbf{r}) &= \mathbf{E}_{\mathrm{Ext}}(\mathbf{r}) + \sum_{j=1}^{N} \int_{V_j} d\mathbf{r}'\, \overleftrightarrow{\mathbf{t}}(\mathbf{r}-\mathbf{r}')\mathbf{P}(\mathbf{r}') \\ &\approx \mathbf{E}_{\mathrm{Ext}}(\mathbf{r}) + \sum_{j=1}^{N} \overleftrightarrow{\mathbf{t}}(\mathbf{r}-\mathbf{r}_j)\mathbf{p}_j \quad (r \notin V) \\ &\approx \mathbf{E}_{\mathrm{Ext}}(\mathbf{r}) + \int_{V_i} d\mathbf{r}'\, \overleftrightarrow{\mathbf{t}}(\mathbf{r}-\mathbf{r}')\mathbf{P}(\mathbf{r}') \\ &\quad + \sum_{j\neq i}^{N} \overleftrightarrow{\mathbf{t}}(\mathbf{r}-\mathbf{r}_j)\mathbf{p}_j \quad (\mathbf{r} \in V_i), \\ \mathbf{p}_j &= \int_{V_j} d\mathbf{r}'\, \mathbf{P}(\mathbf{r}'), \end{aligned} \quad (8)$$

where $V_0 = \Sigma_{i=1}^{N} V_i$ is the total volume occupied by the system. The $\mathbf{p}_j$ are the dipole strengths of the system. The issue of how to choose the cell coordinate $\mathbf{r}_i$ and how to define the cell boundaries will not be treated here. In all practical calculations, which we have performed by means of the discrete cellular method, our choice has been such that each dipole corresponds to exactly one atom and the nuclear coordinate of that atom has been used as the cell coordinate. The cell itself has been of Voronoi type, which means that the interior of the cell belonging to nuclear coordinate $\mathbf{r}_i$, consists of all points which are closer to this coordinate than to any other nuclear coordinate $\mathbf{r}_j$. So the emphasis of the discrete cellular method is on the one atom/one dipole assignment. This choice is considered to be an optimum choice, but has turned out to be problematic for semiconductor systems[13] when using the traditional discrete dipole treatment. As mentioned, cells are also used in chemistry,[1] but the shape is different from the one used by us.

A. Intracellular issues

We will have to approximate the contribution of the polarization density of a cell, say *i*, to the electric field inside the cell itself. This contribution is given by the second term in the third line of Eq. (8) and will be called $\mathbf{E}_{\mathrm{Intra}}(\mathbf{r})$, defined as

$$\mathbf{E}_{\mathrm{Intra}}(\mathbf{r}) = \int_{V_i} d\mathbf{r}'\, \overleftrightarrow{\mathbf{t}}(\mathbf{r}-\mathbf{r}')\mathbf{P}(\mathbf{r}'). \quad (9)$$

Two alternative choices can be made to approximate $\mathbf{E}_{\mathrm{Intra}}$. We either calculate the cell average of the field of a point dipole that is placed in the center $\mathbf{r}_i$ of the cell, or we use the (constant) field in this cell when we assume that the polarization is smeared out uniformly. The first choice results in

$$\begin{aligned} \mathbf{E}_{\mathrm{Intra}}(\mathbf{r}) &\approx \left\langle \int_{V_i} d\mathbf{r}'\, \overleftrightarrow{\mathbf{t}}(\mathbf{r}-\mathbf{r}')\,\delta(\mathbf{r}-\mathbf{r}_i)\mathbf{p}_i \right\rangle \\ &= \frac{1}{V_i}\int_{V_i} d\mathbf{r}''\, \overleftrightarrow{\mathbf{t}}(\mathbf{r}_i-\mathbf{r}'')\mathbf{p}_i. \end{aligned} \quad (10)$$

When the cells are cubic or spherical, this field is equal to the static Lorentz field. The second choice is better calculated directly using methods of electrostatics and yields the same static Lorentz field when the cells are ellipsoids:

$$\mathbf{E}_{\mathrm{Lor,St}} = -\frac{\mathbf{p}_i}{3\epsilon_0 V_i}. \quad (11)$$

Equivalence of these two extreme alternatives provides us with some confidence in the approximations made. From practice we have learned that the energy balance can only be retained when radiation losses are taken into account. This is achieved by including the Lorentz reaction field:

$$\mathbf{E}_{\mathrm{Lor,Rc}} = -\frac{\dddot{\mathbf{p}}_i}{6\pi\epsilon_0 c^3} = \frac{ik^3\mathbf{p}_i}{6\pi\epsilon_0}. \quad (12)$$

We use this approximation of the intracellular field $\mathbf{E}_{\mathrm{Intra}}$ at the cellular coordinate $\mathbf{r}_i$ to define the intracellular transfer tensor $\mathbf{t}_{ii}$ according to

$$\begin{aligned} \mathbf{E}_{\mathrm{Intra}}(\mathbf{r}_i) &= \overleftrightarrow{\mathbf{t}}_{ii}\mathbf{p}_i \\ \overleftrightarrow{\mathbf{t}}_{ii} &= \frac{1}{3\epsilon_0}\left[-\frac{1}{V_i} + \frac{ik^3}{2\pi}\right]\overleftrightarrow{\mathbf{1}}. \end{aligned} \quad (13)$$

The two Lorentz fields have been studied extensively in the literature. There are studies going beyond the point dipole approximation[14] and also the reaction field is still of interest.[15]

B. Nonlocal polarizability concept (quantum induction)

The coupling of the polarization to the electric fields can only be done properly at a microscopic continuum level and is controlled by the nonlocal susceptibility kernel $\chi(\mathbf{r},\mathbf{r}')$:

$$\mathbf{P}(\mathbf{r})=\int \mathbf{dr}'\overleftrightarrow{\chi}(\mathbf{r},\mathbf{r}')\mathbf{E}(\mathbf{r}'). \tag{14}$$

It is this susceptibility which has a direct connection to (microscopic) quantum mechanical descriptions, as shown in Ref. 10. The dipole strength of cell V_i follows now by means of Eq. (8):

$$\mathbf{p}_i=\int_{V_i} d\mathbf{r}'\int d\mathbf{r}''\overleftrightarrow{\chi}(\mathbf{r}',\mathbf{r}'')\mathbf{E}(\mathbf{r}''). \tag{15}$$

This expression can be discretized in a way similar to the discretization of the electric field:

$$\mathbf{p}_i\approx\sum_j \overleftrightarrow{\alpha}_{ij}^{qm}\mathbf{E}_{Av,j},$$
$$\overleftrightarrow{\alpha}_{ij}^{qm}=\int_{V_i} d\mathbf{r}'\int_{V_j} d\mathbf{r}''\overleftrightarrow{\chi}(\mathbf{r}',\mathbf{r}''), \tag{16}$$

where the quantum mechanical nonlocal polarizability α^{qm} gets introduced. With the only purpose to illustrate use in actual calculations, we give the explicit microscopic expression:

$$\overleftrightarrow{\alpha}_{ij}^{qm}(\omega)=\frac{2e^2\hbar^2}{m^2\omega^2}\mathrm{Re}\left[\sum_{n\neq 0}\left(\frac{[\int_{V_i}d\mathbf{r}'\phi_n^*(\mathbf{r}')\nabla'\phi_0(\mathbf{r}')][\int_{V_j}d\mathbf{r}\phi_0^*(\mathbf{r})\nabla\phi_n(\mathbf{r})]^T}{E_0+\hbar\omega-E_n}\right)\right]. \tag{17}$$

This rather tutorial expression results from a highly simplified derivation (see Ref. 16) for a single electron system and comes close to the paramagnetic term in Eq. (4.1) of Ref. 11. It can be extended for many electron systems,[11] by replacing the index 0 by a summation over all occupied levels m. Then the quasienergies E_n and effective one particle wave functions ϕ_n, from any modern electronic structure program (including band structure programs) can be used. Our calculations hitherto have all been of this type. As far as time dependence is concerned this means that technically the present DCM calculations have been of RPA or time-dependent Hartree type. Expression (17) is usable for all materials apart from metals. In principle it should hold also for metals, but for metals the range of quantum mechanical nonlocality is expected to be too large to allow for the direct treatment given in this paper. Pay particular attention to the interplay of the two volumes V_i and V_j and the spatial behavior of the wave functions ϕ_n. A nonzero result will be obtained for $i\neq j$ when the quantum induction criteria elucidated in the introduction will be met. Finally all quantum induction requires from the wave function, is that it is continuous and differentiable, hence it is a very basic property.

The use of nonlocal susceptibilities is known from literature[17] for already a long time. However, in this paper the emphasis is on how nonlocal polarizabilities affect the optical response of surfaces and inhomogeneous systems in general. The average electric field $\mathbf{E}_{\mathrm{Av}}$ is defined as

$$\mathbf{E}_{\mathrm{Av},j}=\mathbf{E}_{\mathrm{Ext},j}+\overleftrightarrow{\mathbf{t}}_{jj}\mathbf{p}_j+\sum_{j'\neq j}^{N}\overleftrightarrow{\mathbf{t}}_{jj'}\mathbf{p}_{j'},$$
$$\mathbf{E}_{\mathrm{Ext},j}=\mathbf{E}_{\mathrm{Ext}}(\mathbf{r}_j), \tag{18}$$
$$\overleftrightarrow{\mathbf{t}}_{jj'}=\overleftrightarrow{\mathbf{t}}(\mathbf{r}_j-\mathbf{r}_{j'}),$$

where now also the intercellular transfer tensors $\mathbf{t}_{jj'}$ have been defined. The common explicit expression for these intercellular transfer tensors is

$$\overleftrightarrow{\mathbf{t}}_{jj'}=\frac{e^{ikr_{jj'}}}{4\pi\epsilon_0}\left[\left(\frac{3}{r_{jj'}^3}-\frac{3ik}{r_{jj'}^2}-\frac{k^2}{r_{jj'}}\right)\hat{\mathbf{r}}_{jj'}\hat{\mathbf{r}}_{jj'}^T+\left(-\frac{1}{r_{jj'}^3}+\frac{ik}{r_{jj'}^2}+\frac{k^2}{r_{jj'}}\right)\overleftrightarrow{\mathbf{1}}\right]\quad(j\neq j'). \tag{19}$$

From here we will refer to both types (intra- and intercellular) commonly as transfer tensors. The definitions for the nonlocal induction [Eq. (16)] and the corresponding definition for the average electric field [Eq. (18)] are the key equations underlying the discrete cellular method (DCM).

In DDM the cells can only be polarized independently. DCM accounts for the quantum induction phenomenon explained in the introduction. It will also cause neighboring cells to get polarized nonlocally. So the dipole strength of a cell will also depend on the perturbing fields in neighboring cells. All neighboring cell contributions need to be added. Quantum induction is nothing else but a physically transparent way to explain the action of nonlocal susceptibility in a cellular description. The second index j of the nonlocal polarizability in Eq. (16) is crucial then. Summation over this index gives the total influence of induction on site i. At first glance this builds only a minor correction of the classical discrete dipole scheme. In practice however the consequences are major. Nonlocal polarizabilities cannot be deduced from experimental data, but can only be obtained through explicit calculation, as will be shown in a forthcoming paper.[11] Furthermore nonlocal polarizabilities turn out to have little influence on homogeneous bulk properties, but they have a decisive influence on inhomogeneous properties.[10]

C. Local versus average fields

For reasons of compatibility with generally accepted descriptions, like the classical discrete dipole method, we have to introduce and discuss the local field $\mathbf{E}_{\mathrm{Loc}}$. The definition is

$$\mathbf{E}_{\mathrm{Loc},i}=\mathbf{E}_{\mathrm{Ext},i}+\sum_{j\neq 1}^{N}\overleftrightarrow{\mathbf{t}}_{ij}\mathbf{p}_j\,. \tag{20}$$

It is trivial to see that this field and the average field are related as

$$\mathbf{E}_{\mathrm{Av},j}=\mathbf{E}_{\mathrm{Loc},j}+\overleftrightarrow{\mathbf{t}}_{jj}\mathbf{p}_j\,. \tag{21}$$

We need the local field, because the classical discrete dipole method, upon which much commonly used expressions are based, expresses induction in a different way:

$$\mathbf{p}_i=\overleftrightarrow{\alpha}_i^{\mathrm{cell}}\mathbf{E}_{\mathrm{Loc},i}\,. \tag{22}$$

In DDM the polarizability is always local (hence it can do with a single index) and it has been given the label ''cell,'' since it incorporates everything taking place inside the cell. Both in DCM and DDM cells can be chosen freely. In practice however cells in DDM mostly contain several atoms and the optimum choice for DCM involves cells containing only one atom. This poses restrictions if we want to compare DDM and DCM results, which becomes necessary if we have to compare the results with experimental data. Comparison is only possible if we use a restricted kind of DCM applicable for local cases only:

$$\mathbf{p}_i=\overleftrightarrow{\alpha}_{ii}^{qm}\mathbf{E}_{\mathrm{Av},i}\,. \tag{23}$$

This local kind of DCM may contain several atoms per cell. A combination of Eqs. (22), (23), and (21) [multiply Eqs. (22), (23) by the inverse polarizability and subtract] yields the following important relation between both kinds of polarizability:

$$\mathbf{t}_{ii}=(\overleftrightarrow{\alpha}_i^{qm})^{-1}-(\overleftrightarrow{\alpha}_{ii}^{\mathrm{cell}})^{-1}. \tag{24}$$

Measured data are always related to cell polarizabilities and calculated data are related to quantum mechanical polarizabilities. Either when using gas-phase data or bulk data obtained by means of Lorentz–Lorenz, this correspondence needs to be checked prior to use.

If induction is nonlocal according to Eq. (16) and we use the average field expression [Eq. (18)] we are dealing with a discrete cellular description. If we combine the local field expression [Eq. (20)] with the local induction [Eq. (22)], we have the classical discrete dipole description. Quantum induction effects introduce through the nonlocal polarizabilities a second (quantum mechanical) kind of nonlocality competing with the previous electric kind of nonlocality, the local field effect of classical DDM. DCM accounts for the electric nonlocality by means of the average electric field and this nonlocality becomes interwoven with the quantum mechanical nonlocality stemming from quantum induction effects. As a result the concept of a local field effect as a stand alone phenomenon is no longer meaningful. For the same reason there is also no such thing as a ''local field correction.'' Correction would mean that the effect is small and can be separated from the rest of the interactions, but this is not the case.

Discrete methods are by their very nature always approximate. The main load of this approximation goes to the intracellular part of the treatment. There in particular the approximation is quite drastic. Nonetheless the results are far better than may have been anticipated, as we have shown in Ref. 10. For the case of GaAs treated in Ref. 10, we focused on surface contributions and we used only a correction of the intracellular transfer tensor of a few % to obtain optimal agreement for the bulk response. The agreement with the experimental reflectance anisotropy was very good, better than for other methods applied to this case. This confirms the validity of the approximations made. Contrary to traditional quantum mechanical treatments of optical properties (RPA, GW, BSE), where the emphasis is on the correct energetic location of features, DCM focuses in the first place on correct intensities of those same features.

Until here we have used the concept of a cell to give the physical basis of the dipole strength $\mathbf{p}_i$ and cellular polarizability. In the remainder of this paper only dipole strengths and polarizabilities will be used and we will not need this cell concept anymore. All cells used hereafter, will be collections (mathematical sets) of discrete dipoles.

III. CLUSTERS

In general the equations governing both discrete dipole and discrete cellular calculations result in a single linear system of equations to be solved. This system can always be written as a matrix equation and, although the form of these equations is not unique, in practice only two types have shown to be really useful. Both representations need composite vectors and matrices. The composite vector $|\mathbf{P}|$ has $3N$ components, taken from the N normal vectors $\mathbf{p}_i$ as:

$$P_{3(i-1)+\xi}=p_{i\xi}\,, \tag{25}$$

where $\xi=1,2,3$ are Cartesian directions. Hereafter any quantity $|\mathbf{P}|$ will refer to a composite vector only. In a similar fashion we define the composite matrix M from its constituent 3×3 subtensors $\mathbf{m}_{ij}$ through:

$$\mathsf{M}_{3(i-1)+\xi,3(j-1)+\eta}=\overleftrightarrow{\mathbf{m}}_{ij,\xi\eta}\,,\quad \xi,\eta=1,2,3. \tag{26}$$

Rather than using this lengthy expression we will use the following shortcut notation (square brackets point to a block part of the matrix):

$$[\mathsf{M}]_{ij}=\overleftrightarrow{\mathbf{m}}_{ij}\,. \tag{27}$$

The shortcut has exactly the same meaning as Eq. (26). So sans serif capitals will refer in this paper to composite matrices. Now we can define for DCM the matrices A and T by:

$$\begin{aligned}[\mathsf{A}]_{ij}&=\overleftrightarrow{\alpha}_{ij}^{qm}\,,\\ [\mathsf{T}]_{ij}&=\overleftrightarrow{\mathbf{t}}_{ij}\,.\end{aligned} \tag{28}$$

A visualization of this polarizability matrix A is shown in Fig. 1 together with the comparable DDM polarizability matrix composed of local cell polarizabilities. This figure shows one of the most significant differences between the two

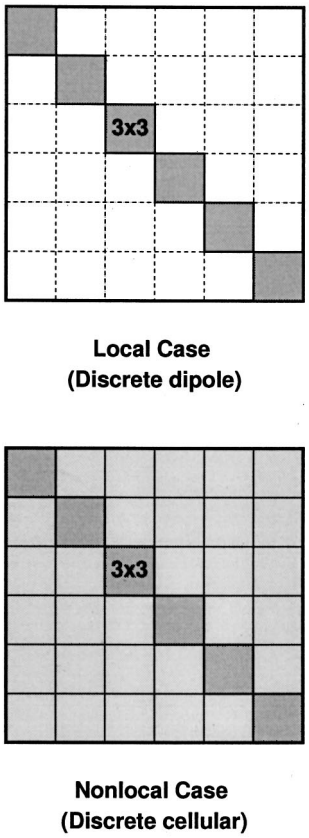

FIG. 1. The local and nonlocal polarizability matrices. The local matrix has nonzero elements only in the diagonal blocks. The nonlocal matrix is completely filled.

methods. In the left panel the DDM polarizability matrix is shown. It contains nonzero block diagonals, and the rest of the matrix is empty. The DCM polarizability matrix shown in the right panel is in general full. Now Eqs. (16) and (18) need to be combined, yielding the most general description of an arbitrary cluster of induced dipoles for the discrete cellular model:

$$|\mathbf{P}| = \mathsf{A}|\mathbf{E}_{\mathrm{Av}}|, \qquad |\mathbf{E}_{\mathrm{Av}}| = |\mathbf{E}_{\mathrm{Ext}}| + \mathsf{T}|\mathbf{P}|. \tag{29}$$

It requires only minor reorganization to see that we need to solve only a single matrix equation, to arrive at the solution of the source terms $\mathbf{p}_i$:

$$[\mathbf{1} - \mathsf{AT}]|\mathbf{P}| = \mathsf{A}|\mathbf{E}_{\mathrm{Ext}}| \tag{30}$$

and its solution, which can be obtained using standard linear algebra routines, can formally be written as

$$|\mathbf{P}| = [\mathbf{1} - \mathsf{AT}]^{-1}\mathsf{A}|\mathbf{E}_{\mathrm{Ext}}|. \tag{31}$$

Once we have solved for the source terms $\mathbf{p}_i$, we still do not have measurable quantities. Those are invariably related to the remote field $\mathbf{E}_{\mathrm{Rem}}$ that is produced by the system of dipoles and which is given for a remote point $\mathbf{R}$ by

$$\mathbf{E}_{\mathrm{Rem}}(\mathbf{R}) = \overleftrightarrow{\mathbf{t}}_R(\mathbf{R})\mathbf{P}_R(\mathbf{R}),$$
$$\overleftrightarrow{\mathbf{t}}_R(\mathbf{R}) = \frac{k^2 e^{ikR}}{4\pi\epsilon_0 R}[\overleftrightarrow{\mathbf{1}} - \hat{\mathbf{R}}\hat{\mathbf{R}}^T], \tag{32}$$
$$\mathbf{P}_R(\mathbf{R}) = \sum_{j=1}^{N} e^{-ik\hat{\mathbf{R}}^T\mathbf{r}_j}\mathbf{p}_j .$$

Here $\overleftrightarrow{\mathbf{t}}_R$ is the remote propagator of the system.

In principle the Eqs. (31) and (32) govern the optical response of an arbitrary cluster of dipoles and these are solvable as long as the size is finite (in practice: as long as the computer can handle it). In general however also (semi)-infinite systems need to be treated, e.g., for the optical reflection problem. As mentioned already, such systems can traditionally only be solved if they obey parallel translational symmetry, which requires the use of special techniques.

IV. STATIC CRYSTALLINE BULK

The nonlocal equivalent of the Lorentz–Lorenz relation requires analysis of a bulk system of dipoles having cubic symmetry and subject to a uniform and static electric field (the full theory given in Sec. VI is dynamical and holds for any crystalline system, including systems which need to be described in a continuum approach by means of an anisotropic bulk dielectric constant). A proper treatment of this case is necessary, since it enables comparison with experimental bulk optical data. The DDM treatment of this case results in the traditional Lorentz–Lorenz expression:

$$\left(\frac{\epsilon - 1}{\epsilon + 2}\right) = \frac{\alpha_B}{3V_{WS}\epsilon_0}, \tag{33}$$

where V_{WS} is the volume of the translationally invariant unit cell (or Wigner–Seitz cell) and ϵ is the relative bulk dielectric constant. It has the common meaning, defined by

$$\langle \mathbf{P} \rangle = (\epsilon - 1)\epsilon_0 \langle \mathbf{E} \rangle, \tag{34}$$

where $\langle \mathbf{P} \rangle$ is the macroscopic (average) polarization and $\langle \mathbf{E} \rangle$ the macroscopic (average) electric field from the macroscopic Maxwell equations. Equation (33) enables us to relate the dielectric constant, measured in a traditional way, to the (experimental) polarizability α_B. This α_B is the cell polarizability of the Wigner–Seitz cell.

To compare this local polarizability α_B, related to a single dipole description (Lorentz–Lorenz), with a DCM derived local polarizability we need a single cell (Wigner–Seitz unit cell) description, as explained in the previous section. Also here the dipole strengths and average electric fields will be the same everywhere as in the Lorentz–Lorenz treatment. Suppose we focus upon an arbitrary dipole and give its site the index 0, then the first result of this (static) symmetry is

$$\mathbf{E}_{\mathrm{Av},j} = \mathbf{E}_{\mathrm{Av},0}, \tag{35}$$

where j is now an arbitrary cell index. If we apply this knowledge to Eq. (16), we find immediately that

$$\mathbf{p}_0=\overleftrightarrow{\alpha}_B^{qm}\mathbf{E}_{\mathrm{Av},0},$$
$$\overleftrightarrow{\alpha}_B^{qm}=\sum_j \overleftrightarrow{\alpha}_{0j}^{qm}. \tag{36}$$

This bulk polarizability $\overleftrightarrow{\alpha}_B^{qm}$ is equivalent to the local polarizability in a local description such as Lorentz–Lorenz. This allows us to use the correspondence (24) to derive the (theoretical) cell polarizability:

$$\overleftrightarrow{\alpha}_B^{\mathrm{cell}}=[(\overleftrightarrow{\alpha}_B^{qm})^{-1}-\overleftrightarrow{\mathbf{t}}_{ii}]^{-1}. \tag{37}$$

For an isotropic bulk system the trace average of this theoretical cell polarizability should be comparable to the experimental bulk polarizability α_B obtained from Eq. (33). The degree of agreement is a test for the DCM description in bulk.

In actual DCM calculations we have used more atoms in the Wigner–Seitz cell, each atom having its own cell. As shown in Ref. 10, we can still use the same technique to compare theoretical and experimental polarizabilities, if we define now for isotropic cases the parameters $\alpha_{\xi\xi}$ ($\xi=1,2,3$):

$$\alpha_{\xi\xi}=\frac{1}{3}\mathrm{Tr}\sum_{i,j}\overleftrightarrow{\alpha}_{ij}^{qm} \tag{38}$$

and use them as the diagonal components of an effective $\overleftrightarrow{\alpha}_B^{\mathrm{cell}}$. (This diagonal value is the α_{Iso} from Ref. 11.) Since quantum mechanical nonlocal and local behavior cannot be distinguished in a system of bulk cubic symmetry, it is impossible to learn about nonlocality from the Lorentz–Lorenz rule. To study nonlocal behavior requires the study of (strongly) inhomogeneous systems, such as surfaces or of spatial dispersion phenomena in the bulk.[18,19]

V. PARALLEL TRANSLATIONAL SYMMETRY

In this section we will treat systems of lower symmetry than the idealized bulk. The description of the dynamic response of a crystalline surface needs the use of parallel translational symmetry. We can always compose such systems starting from regular lattice planes spanned by

$$\mathbf{s}_{n_1,n_2}=n_1\mathbf{s}_1+n_2\mathbf{s}_2. \tag{39}$$

Here $\mathbf{s}_1$ and $\mathbf{s}_2$ are the two planar basis vectors and each $\mathbf{s}_{n_1,n_2}$ corresponds to a cell/nuclear coordinate. For reasons of brevity we will always represent the pair (n_1,n_2) by a single generalized index l. For a static uniform external electric field each site within the plane will be identical. When the system gets exposed to an external field of plane wave type as given by Eq. (7), the situation becomes quite different. There will be a phase difference between the response of a site at $\mathbf{s}_l$ and a site at the origin which is the same as the phase difference of the external field between the same two points. We get as a result

$$\mathbf{U}(\mathbf{s}_l)=\mathbf{U}(\mathbf{0})e^{i\mathbf{k}_\parallel^T\mathbf{s}_l},$$
$$\mathbf{k}=(\mathbf{k}_\parallel,k_\perp), \tag{40}$$

where $\mathbf{k}_\parallel$ is the projection of the incoming wave vector $\mathbf{k}$ onto the plane and $k_\perp$ the component normal to the plane. This is the central equation governing parallel translational symmetry in crystalline lattices and we emphasize its generality. In discrete dipole theory this symmetry is applied to the dipole strength $\mathbf{p}$ only. The discrete cellular method applies this relation to both the dipole strength $\mathbf{p}$ and the average field $\mathbf{E}_{\mathrm{Av}}$.

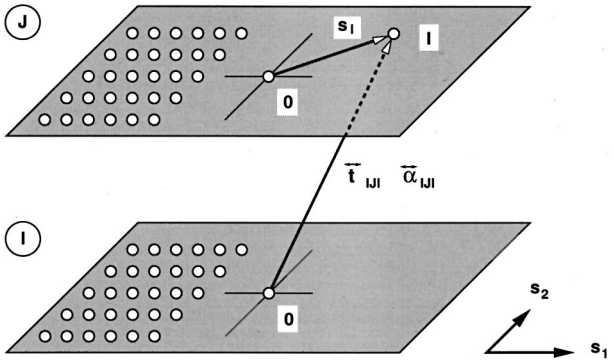

FIG. 2. Two planes of interacting dipoles.

A. Slabs

The translational symmetry relation enables us to treat slab-type systems of infinite extent in the lateral direction, when composed of crystalline lattice planes of the type described above. Different from the discrete dipole case, where we have applied the symmetry rule (40) only to local field expression (20), we have to apply this rule for the discrete cellular case also to the induction expression (16). We start with the average field expression (18):

$$\mathbf{E}_{\mathrm{Av},I}=\mathbf{E}_{\mathrm{Ext},I}+\sum_{J\neq I}\left[\sum_l e^{i\mathbf{k}_\parallel^T\mathbf{s}_l}\overleftrightarrow{\mathbf{t}}_{IJl}\right]\mathbf{p}_J+\left[\sum_{l\neq 0} e^{i\mathbf{k}_\parallel^T\mathbf{s}_l}\overleftrightarrow{\mathbf{t}}_{IIl}\right]\mathbf{p}_I. \tag{41}$$

The following has been done. We select in each plane having capital index I, the **O**-site and call this the characteristic site with the corresponding characteristic dipole $\mathbf{p}_I$. Then we collect the fields caused by the dipoles of the system by first summing within the planes using parallel translational symmetry and then summing over all planes. In this first summation the characteristic dipole can be taken outside and it suffices for the remainder to consider characteristic sites only. The situation is shown in Fig. 2. Now we can reorganize the expression for the average field resulting in

$$\mathbf{E}_{\mathrm{Av},I}=\mathbf{E}_{\mathrm{Ext},I}+\sum_{J\neq I}\overleftrightarrow{\mathbf{f}}_{IJ}\mathbf{p}_J+\overleftrightarrow{\mathbf{f}}_{II}\mathbf{p}_I,$$
$$\overleftrightarrow{\mathbf{f}}_{IJ}=\sum_l e^{i\mathbf{k}_\parallel^T\mathbf{s}_l}\overleftrightarrow{\mathbf{t}}_{IJl},\quad \text{interplanar}, \tag{42}$$
$$\overleftrightarrow{\mathbf{f}}_{II}=\sum_l e^{i\mathbf{k}_\parallel^T\mathbf{s}_l}\overleftrightarrow{\mathbf{t}}_{IIl},\quad \text{intraplanar}.$$

The tensor quantities $\overleftrightarrow{\mathbf{f}}_{IJ}$ and $\overleftrightarrow{\mathbf{f}}_{II}$ are the inter- and intraplanar transfer tensors and have been studied by Litzman,[5,6] by us,[7,8] and several other authors. The transfer tensors provide the main components of the treatment of (semi)-infinite dipole lattices.

The construction of inter- and intraplanar transfer tensors is common to both the discrete dipole and the discrete cellular treatments. A parallel translational symmetry treatment of the induction rule however, is required only for the discrete cellular method which distinguishes it from the former. We start by applying this symmetry to the average field, using Eq. (40):

$$\mathbf{E}_{\mathrm{Av}}(\mathbf{s}_l)=\mathbf{E}_{\mathrm{Av}}(\mathbf{0})e^{i\mathbf{k}_\parallel^T\mathbf{s}_l}. \tag{43}$$

This result we now use in Eq. (16) to obtain

$$\mathbf{p}_I=\sum_J\ \sum_l\ \vec{\alpha}_{IJl}^{qm}\mathbf{E}_{\mathrm{Av},Jl}=\sum_J\left[\sum_l\ \vec{\alpha}_{IJl}^{qm}e^{i\mathbf{k}_\parallel^T\mathbf{s}_l}\right]\mathbf{E}_{\mathrm{Av},J}, \tag{44}$$

where $\mathbf{E}_{\mathrm{Av},J}$ is the average field at the characteristic site J. This can be reorganized into

$$\begin{aligned}\mathbf{p}_I&=\sum_J\ \vec{\alpha}_{IJ}^{Pl}(\mathbf{k})\mathbf{E}_{\mathrm{Av},J},\\ \vec{\alpha}_{IJ}^{Pl}(\mathbf{k})&=\sum_l\ \vec{\alpha}_{IJl}^{qm}e^{i\mathbf{k}_\parallel^T\mathbf{s}_l},\end{aligned} \tag{45}$$

where $\vec{\alpha}^{Pl}$ is the planar polarizability.

The most remarkable result of nonlocality is the **k**-dependent planar polarizability as given in Eq. (45). As before, because of the parallel translational symmetry, each plane can be characterized completely by its characteristic site. Then it is also convenient to consider the characteristic index only and replace the capital index by a more common lower case index. As a result the description for an arbitrary crystalline slab of dipoles becomes identical to the description of an arbitrary cluster of dipoles, but with the constraint that the dipoles can only be located inside the parallel translational unit cell. The only visible difference is in the replacement of the dipole-dipole transfer tensors $\mathbf{t}_{ij}$ by the interplanar transfer tensors $\mathbf{f}_{ij}$ and a corresponding replacement of polarizabilities by planar polarizabilities.

So we define again a polarizability matrix A and a transfer tensor matrix F by

$$\begin{aligned}[\mathsf{A}]_{ij}&=\vec{\alpha}_{ij}^{Pl}(\mathbf{k}),\\ [\mathsf{F}]_{ij}&=\vec{\mathbf{f}}_{ij}(\mathbf{k}).\end{aligned} \tag{46}$$

This yields the general description for an arbitrary crystalline slab system for the discrete cellular method. We only need to solve the matrix equation:

$$[\mathbf{1}-\mathsf{AF}]|\mathbf{P}|=\mathsf{A}|\mathbf{E}_{\mathrm{Ext}}| \tag{47}$$

to arrive at the solution of the source terms $\mathbf{p}_i$ which has to be obtained from

$$|\mathbf{P}|=[\mathbf{1}-\mathsf{AF}]^{-1}\mathsf{A}|\mathbf{E}_{\mathrm{Ext}}|. \tag{48}$$

This equation is suited for slabs, but is still not adequate to deal with semi-infinite systems directly.

VI. SEMI-INFINITE CRYSTALLINE SYSTEMS

Using the same parallel translational symmetry, as used for slabs, semi-infinite crystalline systems can also be treated. A considerable increment in complexity, however, is the price which has to be paid to make this step. The easiest way to see what it is all about, is to start from the slab of the previous section and to put a purely crystalline bulk, obeying the same parallel translational symmetry, underneath. As we will see, it is possible to describe the optical response of this added bulk part by means of so-called normal modes [Eq. (52)]. Although it requires a separate calculation [Eq. (66)] to find these normal modes, their use enables the description of the bulk response by, in general, only two complex numbers. Normal modes completely replace the dielectric constant to describe the bulk optical response. The strength of the method is that it makes a direct link between the microscopic (nonlocal) polarizabilities and the remote optical response, like reflected intensity. From the numerical point of view the bulk behaves as a minor continuation of the surface. A prerequirement to use the normal modes as outlined here, is that the part of the slab which faces the bulk, needs to be of the same geometry and constitution as the bulk. This part functions as a matching layer (the bulklike surface layer of Fig. 4).

This describes in short the double cell technique, introduced by us originally for local (DDM) descriptions.[8] As a guidance tool a flow diagram of the method is given in Fig. 3. The effectiveness of this technique is due to the remnant periodicity along the surface normal some distance below the surface itself. This periodicity reflects the geometric bulk periodicity, where the (characteristic) dipole sites $\mathbf{r}_{vV}$ are given by

$$\mathbf{r}_{vV}=\mathbf{r}_v^B+\mathbf{d}_S+V\mathbf{s}_3. \tag{49}$$

This holds for all dipole sites outside the surface slab. V is the bulk unit cell index. The first bulk unit cell occurs for $V=0$ and has its origin at $\mathbf{d}_S=\mathbf{d}_S^f+N_S^B\mathbf{s}_3$. All N_B dipoles of a bulk unit cell have sites $\mathbf{r}_v^B$ within that cell. The index v runs from 1 to N_B. The semi-infinite lattice is entirely composed of planes obeying the same parallel translational symmetry, as described before. The vector $\mathbf{s}_3$ builds the bulk lattice together with $\mathbf{s}_1$ and $\mathbf{s}_2$. Some comment needs to be given to the composition of the surface cell (indicated with slightly darker shading in Fig. 4). In total there are N_S dipoles in this cell. The surface layer itself is split into two (Fig. 4): a free surface layer (cell) and a bulklike surface layer (cell). In the free surface layer the dipole sites have to obey only parallel translational symmetry. The bulklike surface cell consists of N_S^B bulk unit cells and all dipole positions obey Eq. (49). The bulklike surface layer accounts for the matching of bulk and surface. Numerically (the software package where the contents of this paper have been implemented), all dipoles being in the surface layer (free and bulklike) are treated the same way.

For the double cell technique, we need to consider two kinds of dipoles: bulk dipoles and surface dipoles. For each it will be shown that the double cell technique can handle also nonlocal problems, provided that the range of nonlocality is finite. This range will be governed by Y, the number of bulk unit cells above or below the bulk cell of interest, affected by the (quantum mechanical) nonlocality. The geometric details relevant for the double cell technique are shown in Fig. 4.

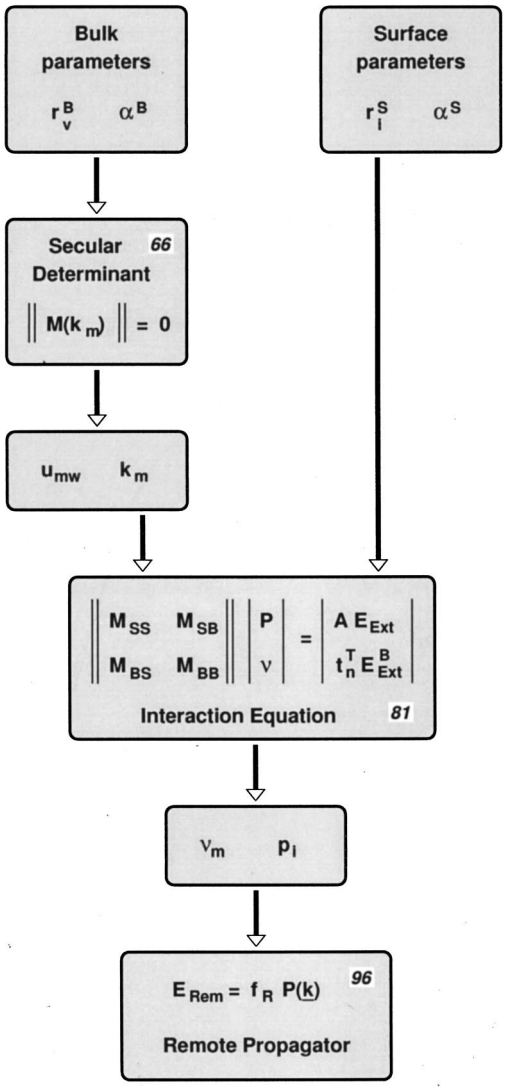

FIG. 3. Flow diagram nonlocal double cell method. Numbers refer to equations in text.

A. Bulk dipoles

We start with the vVth bulk dipole, for which the induction relation is given by

$$\mathbf{p}_{vV} = \sum_{X=V-Y}^{V+Y} \sum_{x=1}^{N_B} \overleftrightarrow{\alpha}^{B,Pl}_{vVxX}(\mathbf{k}) \mathbf{E}_{\mathrm{Av},xX}. \tag{50}$$

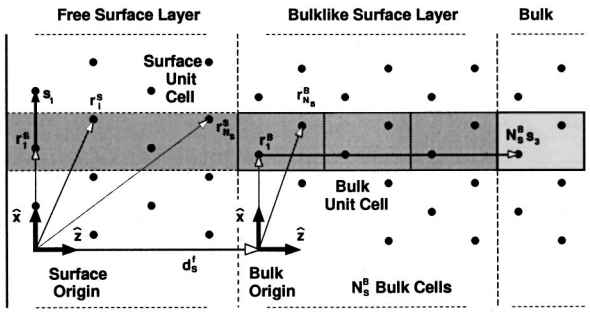

FIG. 4. The double cell geometry: details.

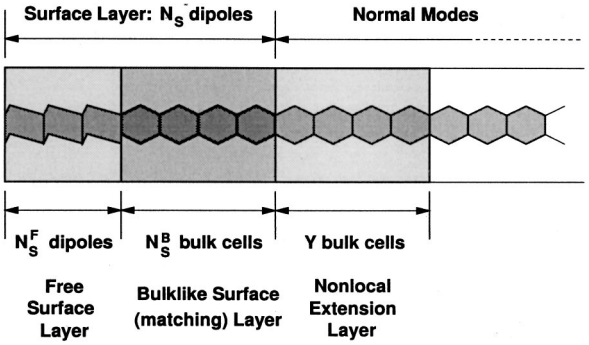

FIG. 5. The quantum mechanical nonlocality and the semi-infinite case.

The polarizabilities $\overleftrightarrow{\alpha}^{B,Pl}_{vVxX}(\mathbf{k})$ each obey Eq. (45). It is implicitly understood, that V exceeds the value of the nonlocal bulk range Y for the bulk (see Fig. 4), so the site considered is not in the nonlocal extension layer (see Fig. 5). Since Eq. (50) has to hold for any bulk site, this imposes no limitation. Further we will use the convention, that for a double pair of indices $vVwW$ the capital indices will be omitted when they are the same. The expression for the bulk average field is given by

$$\mathbf{E}_{\mathrm{Av},xX} = E_0 \hat{\mathbf{e}} e^{i\mathbf{k}^T \mathbf{r}_{xX}} + \sum_{j=1}^{N_S} \overleftrightarrow{\mathbf{f}}_{xXj} \mathbf{p}_j + \sum_{w=1}^{N_B} \left[\sum_{W=0}^{X-1} \overleftrightarrow{\mathbf{f}}_{xXuW} \mathbf{p}_{wW} + \overleftrightarrow{\mathbf{f}}_{xw} \mathbf{p}_{wX} + \sum_{W=X+1}^{\infty} \overleftrightarrow{\mathbf{f}}_{xXwW} \mathbf{p}_{wW} \right]. \tag{51}$$

To evaluate Eq. (51) properly, the use of the remnant bulk perpendicular periodicity is required. This is exploited by using normal modes, defined for each site vV by

$$\mathbf{p}_{vV} = \sum_{m=1}^{M} \nu_m \mathbf{u}_{mv} e^{iV\mathbf{k}_m^T \mathbf{s}_3}. \tag{52}$$

The number of normal modes is given by M. The normal mode strength is ν_m, the normal mode vector is $\mathbf{u}_{mv}$ (a composite vector covering all sites of the bulk unit cell) and the normal mode wave vector is $\mathbf{k}_m$. Note that the normal mode strength ν_m in the above definition is dimensionless. Next the expansion of the planar transfer tensor by means of Ewald's threefold integral transform is indispensable. The expression is given in Ref. 8. This transform and the normal mode expansion decompose the expression for the average field Eq. (51) into ''channels,'' belonging to the wave vectors $\mathbf{k}$, $\mathbf{k}_{q_1q_2}$, and $\mathbf{k}_m$. The partial wave vectors $\mathbf{k}_{q_1q_2}$ have been introduced in Ref. 8 as

$$\begin{aligned} \mathbf{k}_{q_1q_2} &= (\mathbf{k}_\parallel, \kappa_{q_1q_2}), \\ \kappa_{q_1q_2} &= \sqrt{k^2 - (\mathbf{k}_\parallel + \mathbf{g}^\parallel_{q_1q_2})^2}. \end{aligned} \tag{53}$$

Here $\mathbf{g}^\parallel_{q_1q_2}$ is a surface reciprocal lattice vector belonging to the 2D lattice spanned by $\mathbf{s}_{n_1,n_2}$, q_1 and q_2 are integers, and $\mathbf{g}_1$ and $\mathbf{g}_2$ are planar reciprocal lattice basis vectors, given by

$$\mathbf{g}^{\parallel}_{q_1q_2}=q_1\mathbf{g}_1+q_2\mathbf{g}_2,$$
$$\mathbf{g}_1=\left(\frac{2\pi}{s_{1x}},0\right),\tag{54}$$
$$\mathbf{g}_2=\left(-\frac{2\pi s_{2x}}{s_{1x}s_{2y}},\frac{2\pi}{s_{2y}}\right),$$

where we have assumed that $\mathbf{s}_1$ is in the x-direction. For reasons of brevity, we will replace the pair (q_1,q_2) by a single index q. In Eq. (53), on purpose only, the positive solution of the square root has been used to define κ_q. The partial wave vectors $\mathbf{k}_q$ govern the plane wave decomposition of the field emanating from a single crystalline plane of dipoles.[8] Technically there also exists a negative solution for the κ_q, but we have incorporated this sign in the theory such that the partial waves belonging to the $\mathbf{k}_q$, always leave the plane by which they are emitted. For this purpose we have made use of the reflected counterpart $\underline{\mathbf{a}}$ of a vector $\mathbf{a}$ defined as

$$\underline{\mathbf{a}}=(a_x,a_y,-a_z).\tag{55}$$

This means also that when κ_q becomes imaginary (this is always the case in the optical regime apart from $q=00$), the field always decays in a direction away from the plane. After some lengthy, but straightforward derivation, we obtain

$$\mathbf{E}_{\mathrm{Au},xX}=\mathbf{E}^x_{\mathrm{Ext}}(\mathbf{k})e^{iX\mathbf{k}^T\mathbf{s}_3}+\sum_q^{\infty}\mathbf{E}^x_{>}(\mathbf{k}_q)e^{iX\mathbf{k}_q^T\mathbf{s}_3}+\sum_{m=1}^{M}\mathbf{E}^x_B(\mathbf{k}_m)e^{iX\mathbf{k}_m^T\mathbf{s}_m}.\tag{56}$$

The meaning of the channel fields $\mathbf{E}^x_{\mathrm{Ext}}(\mathbf{k})$, $\mathbf{E}^x_{>}(\mathbf{k}_q)$, and $\mathbf{E}^x_B(\mathbf{k}_m)$ is that each of them is controlled by a different exponential of X. They are defined as

$$\mathbf{E}^x_{\mathrm{Ext}}(\mathbf{k})=E_0\hat{\mathbf{e}}e^{i\mathbf{k}^T(\mathbf{r}_x^B+\mathbf{d}_S)},$$
$$\mathbf{E}^x_{>}(\mathbf{k}_q)=\left[\sum_{j=1}^{N_S}e^{i\mathbf{k}_q^T(\mathbf{r}_x^B+\mathbf{d}_S-\mathbf{r}_j)}\overleftrightarrow{\mathbf{d}}_q\mathbf{p}_j+\sum_{w=1}^{N_B}\sum_{m=1}^{M}\nu_m\overleftrightarrow{\mathbf{d}}_q\mathbf{u}_{mw}\left[\frac{e^{i\mathbf{k}_q^T(\mathbf{r}_x^B-\mathbf{r}_w^B)}}{1-e^{i(\mathbf{k}_m-\mathbf{k}_q)^T\mathbf{s}_3}}\right]\right],\tag{57}$$
$$\mathbf{E}^x_B(\mathbf{k}_m)=\nu_m\sum_{w=1}^{N_B}\left[\overleftrightarrow{\mathbf{f}}_{xw}+\sum_q^{\infty}\left[\frac{e^{i\mathbf{k}_q^T(\mathbf{r}_x^B-\mathbf{r}_w^B)}}{e^{i(\mathbf{k}_m-\mathbf{k}_q)^T\mathbf{s}_3}-1}\overleftrightarrow{\mathbf{d}}_q+\frac{e^{i\mathbf{k}_q^T(\mathbf{r}_x^B-\mathbf{r}_w^B)}}{e^{i(\underline{\mathbf{k}}_q-\mathbf{k}_m)^T\mathbf{s}_3}-1}\overleftrightarrow{\mathbf{d}}_q\right]\right]\mathbf{u}_{mw}.$$

The transverse projectors $\overleftrightarrow{\mathbf{d}}_q$ are defined as (for details see Ref. 8)

$$\overleftrightarrow{\mathbf{d}}_q=\frac{i}{2\epsilon_0|\mathbf{s}_1\times\mathbf{s}_2|}\frac{k^2\overleftrightarrow{\mathbf{1}}-\mathbf{k}_q\mathbf{k}_q^T}{\kappa_q}.\tag{58}$$

Using the shorthand notation given in Eq. (56), we can perform the substitution of the average fields in the induction Eq. (50). It will turn out to be convenient to replace the index X by the choice $V+X$. We obtain

$$\sum_{m=1}^{M}\nu_m\mathbf{u}_{mv}e^{iV\mathbf{k}_m^T\mathbf{s}_3}=\sum_{X=-Y}^{+Y}\sum_{x=1}^{N_B}\overleftrightarrow{\alpha}^{B,Pl}_{vVx(V+X)}(\mathbf{k})\times\left[\mathbf{E}^x_{\mathrm{Ext}}(\mathbf{k})e^{i(V+X)\mathbf{k}^T\mathbf{s}_3}+\sum_q^{\infty}\mathbf{E}^x_{>}(\mathbf{k}_q)e^{i(V+X)\mathbf{k}_q^T\mathbf{s}_3}+\sum_{m=1}^{M}\mathbf{E}^x_B(\mathbf{k}_m)e^{i(V+X)\mathbf{k}_m^T\mathbf{s}_3}\right].\tag{59}$$

In order to continue, it is good to define nonlocal bulk polarizabilities as

$$\overleftrightarrow{\alpha}^Y_{vx}(\mathbf{k})=\sum_{X=-Y}^{+Y}\overleftrightarrow{\alpha}^{B,Pl}_{vVx(V+X)}(\mathbf{k})e^{iX\mathbf{k}^T\mathbf{s}_3}=\sum_{X=-Y}^{+Y}\overleftrightarrow{\alpha}^{B,Pl}_{vxX}(\mathbf{k})e^{iX\mathbf{k}^T\mathbf{s}_3}.\tag{60}$$

The index V can be dropped in the previous expression on symmetry grounds. Now it is not difficult to obtain the equation giving the total nonlocal induction onto the vth dipole:

$$\sum_{m=1}^{M}\nu_m\mathbf{u}_{mv}e^{iV\mathbf{k}_m^T\mathbf{s}_3}=\sum_{x=1}^{N_B}\left[\overleftrightarrow{\alpha}^Y_{vx}(\mathbf{k})\mathbf{E}^x_{\mathrm{Ext}}(\mathbf{k})e^{iV\mathbf{k}^T\mathbf{s}_3}+\sum_q^{\infty}\overleftrightarrow{\alpha}^Y_{vx}(\mathbf{k}_q)\mathbf{E}^x_{>}(\mathbf{k}_q)e^{iV\mathbf{k}_q^T\mathbf{s}_3}+\sum_{m=1}^{M}\overleftrightarrow{\alpha}^Y_{vx}(\mathbf{k}_m)\mathbf{E}^x_B(\mathbf{k}_m)e^{iV\mathbf{k}_m^T\mathbf{s}_3}\right].\tag{61}$$

This is an important result as it shows the influence of nonlocality on the double cell description. The difference with respect to the original local description is mainly a modification of the polarizability. In the local description we were dealing with one, $\mathbf{k}$-independent bulk polarizability matrix. Now for the nonlocal case we are left with many $\mathbf{k}$-dependent bulk polarizability matrices. The overwhelming majority of these matrices will disappear in the final description and only a few, decided by the number of required normal modes (usually two), will remain. The next step in the derivation is similar to the previous local derivation: filtering out the independent channels. In total we obtain N_B independent vector equations from Eq. (61) by varying the index v. All coefficients belonging to corresponding channels have to satisfy these equations separately.

As yet the key normal mode parameters (normal mode vector $\mathbf{u}_{mv}$ and wave vector $\mathbf{k}_m$) are not known. We can find them by focusing on the $\mathbf{k}_m$-channel:

$$\nu_m\mathbf{u}_{mv}=\sum_{x=1}^{N_B}\overleftrightarrow{\alpha}^Y_{vx}(\mathbf{k}_m)\mathbf{E}^x_B(\mathbf{k}_m).\tag{62}$$

Now we use Eq. (57) to obtain an explicit expression for the channel fields. The common factor ν_m can be divided out and we obtain

$$\mathbf{u}_{mv}=\sum_{x=1}^{N_B}\vec{\mathsf{A}}_{vx}(\mathbf{k}_m)\sum_{w=1}^{N_B}\left[\vec{\mathbf{f}}_{xw}+\sum_{q}^{\infty}\left[\frac{e^{i\mathbf{k}_q^T(\mathbf{r}_x^B-\mathbf{r}_w^B)}}{e^{i(\mathbf{k}_m-\mathbf{k}_q)^T\mathbf{s}_3}-1}\vec{\mathbf{d}}_q+\frac{e^{i\underline{\mathbf{k}}_q^T(\mathbf{r}_x^B-\mathbf{r}_w^B)}}{e^{i(\underline{\mathbf{k}}_q-\mathbf{k}_m)^T\mathbf{s}_3}-1}\vec{\underline{\mathbf{d}}}_q\right]\right]\mathbf{u}_{mw}, \tag{63}$$

where we introduce the auxiliary $N_B\times N_B$ composite matrix A as

$$[\mathsf{A}(\mathbf{k})]_{vx}=\vec{\alpha}_{vx}^{Y}(\mathbf{k}). \tag{64}$$

Now we can also define a second $N_B\times N_B$ composite (dyadic) matrix F as

$$\mathsf{F}_{xw}(\mathbf{k})=\vec{\mathbf{f}}_{xw}+\sum_{q}^{\infty}\left[\frac{e^{i\mathbf{k}_q^T(\mathbf{r}_x^B-\mathbf{r}_w^B)}}{e^{i(\mathbf{k}-\mathbf{k}_q)^T\mathbf{s}_3}-1}\vec{\mathbf{d}}_q+\frac{e^{i\underline{\mathbf{k}}_q^T(\mathbf{r}_x^B-\mathbf{r}_w^B)}}{e^{i(\underline{\mathbf{k}}_q-\mathbf{k})^T\mathbf{s}_3}-1}\vec{\underline{\mathbf{d}}}_q\right]. \tag{65}$$

After introduction of these two matrices, it is just a minor step to see that Eq. (63) can also be written as the matrix equation:

$$\mathsf{M}(\mathbf{k}_m)|\mathbf{u}|=[\mathbf{1}-\mathsf{A}(\mathbf{k}_m)\mathsf{F}(\mathbf{k}_m)]|\mathbf{u}|=|\mathbf{0}|, \tag{66}$$

where the matrix $\mathsf{M}(\mathbf{k}_m)$ is called the bulk secular matrix. The roots $\mathbf{k}_m$ of secular determinant $\|\mathsf{M}(\mathbf{k}_m)\|$ and, for each $\mathbf{k}_m$, the corresponding normal mode vectors $\mathbf{u}_{mw}$ will determine all normal mode parameters with the exception of the normal mode strength ν_m. This procedure turns out to be exactly the same as for the local case, apart from the occurrence of a more complicated polarizability matrix.

The normal mode vectors $\mathbf{k}_m$, as they are found from Eq. (66), have a clear physical meaning. They govern the bulk material response of the lattice upon the external field [Eq. (7)] and come very close in value to the Fresnel wave vectors from classical optics. They can be used to approximate the (dynamical) continuum dielectric constant $\epsilon(\mathbf{k}_m,\omega)$ to first order by

$$k_m^2=\frac{\omega^2\epsilon(\mathbf{k}_m,\omega)}{c^2}. \tag{67}$$

To extend this relationship beyond the case of a simple uniform isotropic, bulk ends up in a discussion about the relationship between continuum and discrete descriptions (as given here). This discussion is beyond the scope of this paper. Part of the problem can already be seen from the fact that the normal mode vectors $\mathbf{u}_{mw}$ are not accounted for by Eq. (67). We hope to deal with this important issue in a future publication.

We only needed information about the $\mathbf{k}_m$-channel to construct the bulk secular matrix/determinant and to get the normal mode parameters $\mathbf{k}_m$ and $\mathbf{u}_{mw}$. We need an additional set of equations to get the normal mode strengths ν_m. Such a set is produced by the $\mathbf{k}_{00}$-channel of Eq. (56), which as mentioned already in Ref. 8, happens to coincide with the $\mathbf{k}$-channel. From this forward propagating channel we obtain

$$\sum_{x=1}^{N_B}\vec{\alpha}_{vx}^{Y}(\mathbf{k})[\mathbf{E}_{\mathrm{Ext}}^{x}(\mathbf{k})+\mathbf{E}_{>}^{x}(\mathbf{k})]=0. \tag{68}$$

This equation can be recognized again as a matrix equation, being

$$\mathsf{A}(\mathbf{k})|\mathbf{E}_{\mathrm{Ext}}(\mathbf{k})+\mathbf{E}_{>}(\mathbf{k})|=|\mathbf{0}|. \tag{69}$$

If the matrix $\mathsf{A}(\mathbf{k})$ is not singular (which is reasonable since, in general, this matrix is diagonally dominant), we can conclude immediately that

$$|\mathbf{E}_{\mathrm{Ext}}(\mathbf{k})+\mathbf{E}_{>}(\mathbf{k})|=|\mathbf{0}|. \tag{70}$$

This result, which follows so easily if the equations are formulated using the channel fields, is simply the Ewald–Oseen extinction theorem. Focusing on the xth element of this composite vector equation, we perform as a next step the substitutions as required by Eq. (57). As in Ref. 8, however, a common phase factor $\exp(i\mathbf{k}\mathbf{r}_x^B)$ can be divided out. As a result we obtain only a single vector equation, since after division all N_B vector equations in Eq. (70) become identical:

$$-\vec{\mathbf{d}}_{00}\left[\sum_{w=1}^{N_B}\sum_{m=1}^{M}\nu_m\mathbf{u}_{mw}\left[\frac{e^{-i\mathbf{k}^T\mathbf{r}_w^B}}{1-e^{i(\mathbf{k}_m-\mathbf{k})^T\mathbf{s}_3}}\right]+\sum_{j=1}^{N_S}e^{i\mathbf{k}^T(\mathbf{d}_S-\mathbf{r}_j)}\mathbf{p}_j\right]=E_0\hat{\mathbf{e}}e^{i\mathbf{k}^T\mathbf{d}_S}. \tag{71}$$

Apart from some minor differences this result is the same as obtained before in Ref. 8. So nonlocality essentially changes nothing in the bulk part of the double cell interaction equations. All further processing goes along the same lines as given before and we only repeat the result. The cumulative normal mode dipole strength $\mathbf{P}_m^B(\mathbf{k})$ is given by

$$\mathbf{P}_m^B(\mathbf{k})=\frac{\Sigma_{w=1}^{N_B}e^{-i\mathbf{k}^T\mathbf{r}_w^B}\mathbf{u}_{mw}}{1-e^{(i[\mathbf{k}_m-\mathbf{k}]^T\mathbf{d}_B)}}. \tag{72}$$

We need to project onto two orthogonal directions, generically denoted as $\hat{\mathbf{t}}$, where $\hat{\mathbf{t}}$ has to be perpendicular to $\mathbf{k}$, since Eq. (71) is dependent in the direction parallel to $\mathbf{k}$. These directions correspond with the *s*- and *p*-directions in classical optics. We obtain the result for the forward bulk part of the double cell equations:

$$\frac{ik^2}{2\epsilon_0|\mathbf{s}_1\times\mathbf{s}_2||k_z|}\left[-\sum_{m=1}^{M}(\hat{\mathbf{t}}^T\mathbf{P}_m^B(\mathbf{k}))\nu_m-\sum_{j=1}^{N_S}e^{i\mathbf{k}^T(\mathbf{d}_S-\mathbf{r}_j)}\hat{\mathbf{t}}^T\mathbf{p}_j\right]=E_0e^{i\mathbf{k}^T\mathbf{d}_S}(\hat{\mathbf{t}}^T\hat{\mathbf{e}}). \tag{73}$$

That this result happens to be identical for local and nonlocal cases is obvious since nonlocality affects primarily the polarizability matrix, which drops out from the equations already at a very early stage (see Fig. 6).

B. Surface dipoles

Nonlocality affects surface dipoles in a more outspoken way than bulk dipoles. Indeed the complexity of the calculation increases here considerably. Observe in more detail Figs. 5 and 6. As compared to the local cases, the difference

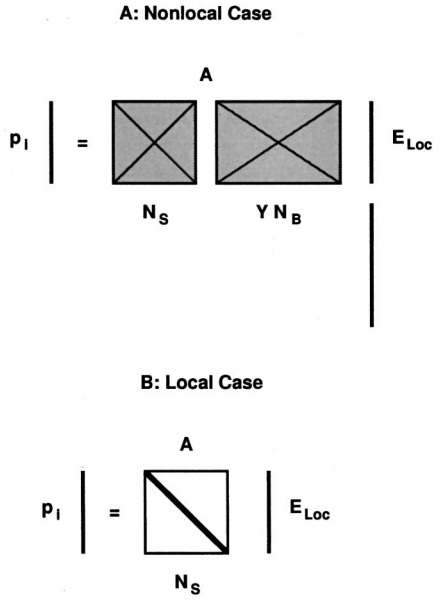

FIG. 6. Comparison for the surface part of the interaction equations for nonlocal (a) and local cases (b).

is in the first Y bulk unit cells of the normal mode region, called the nonlocal extension layer. These cells have now a direct influence on the dipoles of the surface layer. We consider an arbitrary dipole $\mathbf{p}_i$ located in the surface layer and apply the nonlocal induction rule [Eq. (45)]:

$$\mathbf{p}_i=\sum_{l=1}^{N_S}\vec{\alpha}_{il}(\mathbf{k})\mathbf{E}_{\mathrm{Av},l}+\sum_{X=0}^{Y}\sum_{x=1}^{N_B}\vec{\alpha}_{ixX}(\mathbf{k})\mathbf{E}_{\mathrm{Av},xX}. \tag{74}$$

To appreciate things, it is best to write Eq. (74) immediately in matrix form in the manner used before:

$$|\mathbf{P}|=\mathsf{A}(\mathbf{k})|\mathbf{E}_{\mathrm{Av}}|. \tag{75}$$

Special attention needs to be paid to the dimensions. The dipole vector contains N_S vectors, the matrix $N_S\times(N_S+Y*N_B)$ subtensors and the average field vector N_S+Y*N_B vectors (see Fig. 6). In this description all we have to do is focus upon the average field vector and preferably bring it into a compatible matrix notation. This average field vector contains two parts: the average fields belonging to the surface layer and the average fields belonging to the nonlocal extension layer. The surface average fields are in principle given in Ref. 8 and can be repeated in a slightly different notation as

$$\mathbf{E}_{\mathrm{Av},l}=E_0\hat{\mathbf{e}}e^{i\mathbf{k}^T\mathbf{r}_l}+\sum_{j=1}^{N_S}\vec{\mathbf{f}}_{lj}\mathbf{p}_j+\sum_{m=1}^{M}\mathbf{h}_{lm}\nu_m,$$
$$\underline{\mathbf{h}}_{lm}=\sum_{w=1}^{N_B}\sum_{q}^{\infty}\left[\frac{e^{i\underline{\mathbf{k}}_q^T(\mathbf{r}_l-\mathbf{r}_w^B-\mathbf{d}_S)}}{1-e^{i(\mathbf{k_m}-\underline{\mathbf{k}}_q)^T\mathbf{s}_3}}\right]\vec{\mathbf{d}}_q\mathbf{u}_{mw}. \tag{76}$$

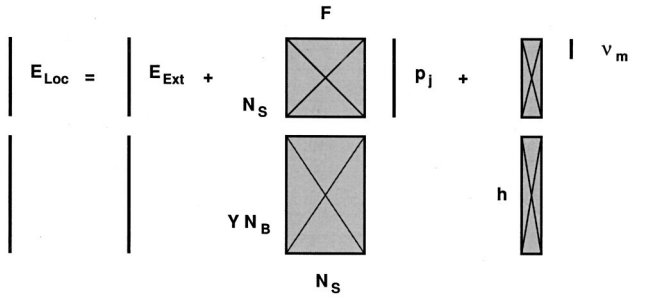

FIG. 7. Schematic view of the surface local field.

Next we need the average field for a dipole located in the nonlocal extension layer. Those are bulk sites entirely located within the normal mode region and in principle we can use Eqs. (56) and (57) directly. A different notation however will make it easier to use these results here:

$$\mathbf{E}_{\mathrm{Av},xX}=E_0\hat{\mathbf{e}}e^{i\mathbf{k}^T[\mathbf{r}_x^B+\mathbf{d}_S+X\mathbf{s}_3]}+\sum_{j=1}^{N_S}\vec{\mathbf{f}}_{xXj}\mathbf{p}_j+\sum_{m=1}^{M}\mathbf{h}_{xXm}\nu_m, \tag{77}$$
$$\mathbf{h}_{xXm}=e^{iX\mathbf{k}_m^T\mathbf{s}_3}\sum_{w=1}^{N_B}\Bigg[\vec{\mathbf{f}}_{xw}+\sum_{q}^{\infty}\Bigg[\left[\frac{e^{i\mathbf{k}_q^T(\mathbf{r}_x^B-\mathbf{r}_w^B)}(e^{iX(\mathbf{k}_q-\mathbf{k}_m)^T\mathbf{s}_3}-1)}{1-e^{i(\mathbf{k}_m-\mathbf{k}_q)^T\mathbf{s}_3}}\right]\vec{\mathbf{d}}_q+\left[\frac{e^{i\underline{\mathbf{k}}_q^T(\mathbf{r}_x^B-\mathbf{r}_w^B)}}{e^{i(\underline{\mathbf{k}}_q-\mathbf{k}_m)^T\mathbf{s}_3}-1}\right]\vec{\mathbf{d}}_q\Bigg]\Bigg]\mathbf{u}_{mw}. \tag{77}$$

Both Eqs. (76) and (77) can be combined and written as a single matrix expression:

$$|\mathbf{E}_{\mathrm{Av}}|=|\mathbf{E}_{\mathrm{Ext}}|+\mathsf{F}|\mathbf{P}|+\mathsf{H}\boldsymbol{\nu}, \tag{78}$$

where H is a composite matrix and matrix F is as defined in Eq. (46). Vector $\boldsymbol{\nu}$ has the M complex numbers ν_m as its components. The size of composite vectors $|\mathbf{E}_{\mathrm{Av}}|$ and $|\mathbf{E}_{\mathrm{Ext}}|$ is N_S+Y*N_B vectors. Composite vector $|\mathbf{P}|$ contains N_S vectors. The dimensions of the matrices are in agreement with those of the vectors. Schematically the situation is shown in Fig. 7. Now it suffices to combine the vector/matrix Eqs. (75) and (78) to arrive at an expression for the induction of a surface dipole,

$$|\mathbf{P}|=\mathsf{A}(\mathbf{k})[|\mathbf{E}_{\mathrm{Ext}}|+\mathsf{F}|\mathbf{P}|+\mathsf{H}\boldsymbol{\nu}], \tag{79}$$

which needs only minor reorganization to produce the form used by us in the nonlocal double cell interaction equations:

$$[\mathbf{1}-\mathsf{A}(\mathbf{k})\mathsf{F}]|\mathbf{P}|-\mathsf{A}(\mathbf{k})\mathsf{H}\boldsymbol{\nu}=\mathsf{A}(\mathbf{k})|\mathbf{E}_{\mathrm{Ext}}|. \tag{80}$$

This result comes very close in form to the expression used for the double cell interaction matrix derived in Ref. 8 for the purely local case. We point out the differences. No explicit inverse of the polarizability matrix occurs and the inhomogeneous vector contains $\mathsf{A}\mathbf{E}_{\mathrm{Ext}}$ instead of $\mathbf{E}_{\mathrm{Ext}}$. The composite matrix $\mathbf{1}-\mathsf{AF}$ is a square matrix of $N_S\times N_S$ subtensors and fills out the *SS*-part of the nonlocal double cell interaction matrix, as before. It is by far the largest part of this matrix. It suffices to combine Eqs. (73) and (80) to give the full interaction matrix M of the nonlocal double cell method:

$$\begin{Vmatrix} \mathsf{M}_{SS} & \mathsf{M}_{SB} \\ \mathsf{M}_{BS} & \mathsf{M}_{BB} \end{Vmatrix} \begin{vmatrix} \mathbf{P} \\ \boldsymbol{\nu} \end{vmatrix} = \begin{vmatrix} \mathsf{A}\mathbf{E}_{\mathrm{Ext}} \\ \mathbf{t}_n^T \mathbf{E}_{\mathrm{Ext}}^B \end{vmatrix}. \tag{81}$$

The dimension of the matrices used here, are exactly as in Ref. 8. The explicit expressions for the components of the matrix are given by

$$\mathsf{M}_{SS} = \mathbf{1} - \mathsf{A}(\mathbf{k})\mathsf{F}, \tag{82}$$

$$\mathsf{M}_{SB} = -\mathsf{A}(\mathbf{k})\mathsf{H}, \tag{83}$$

$$\mathsf{M}_{BS,nj} = \gamma(\mathbf{k})\hat{\mathbf{t}}_n^T, \tag{84}$$

$$\mathsf{M}_{BB,nm} = \gamma(\mathbf{k})\hat{\mathbf{t}}_n^T \mathbf{P}_m^B(\mathbf{k}), \tag{85}$$

where the symbol $\gamma(\mathbf{k})$ is defined by

$$\gamma(\mathbf{k}) = \frac{ik^2}{2\epsilon_0 |\mathbf{s}_1 \times \mathbf{s}_2||k_z|}. \tag{86}$$

For a precise meaning of the further symbols in the nonlocal double cell equations [Eq. (81)], one should revert to the derivation of the basic Eqs. (73) and (80). It is surprising that, although quantum induction heavily perturbs the derivation, the final result is quite manageable and only slightly more complicated than the local case.

C. Extra normal modes

In our previous publications[7,8] we have used the double cell method for the local case (the thick slab method[20] can be seen as an extension of this method). In these previous publications it has always been sufficient to take into account just two normal modes for the bulk region. These two normal modes happened to occur systematically in the close vicinity of the Fresnel solutions (the refracted rays of classical optics). Unexpectedly, while doing calculations on GaAs,[10] it turned out that sometimes more modes were required. These modes will be called extra normal modes and require a somewhat different strategy and treatment to be incorporated. Details will be given here.

To incorporate more normal modes requires extension of the double cell matrix by an additional number of normal modes, all derived from Eq. (66). Apart from the $q=00$ channel we have used before [Eq. (69)], we have to consider also a number of $q \neq 00$ channels. Using the full bulk Eq. (61), we arrive for each q channel at the equation:

$$\mathsf{A}(\mathbf{k}_q)|\mathbf{E}_>(\mathbf{k}_q)| = |\mathbf{0}|. \tag{87}$$

Since we assume again that all matrices $\mathsf{A}(\mathbf{k}_q)$ will be in general nonsingular, we have again

$$|\mathbf{E}_>(\mathbf{k}_q)| = |\mathbf{0}|. \tag{88}$$

By taking the expression for $\mathbf{E}_>^x(\mathbf{k}_q)$ from Eq. (57), we arrive at

$$\sum_{j=1}^{N_S} e^{i\mathbf{k}_q^T(\mathbf{r}_x^B + \mathbf{d}_S - \mathbf{r}_j)} \overleftrightarrow{\mathbf{d}}_q \mathbf{p}_j + \sum_{m=1}^{M} \nu_m \overleftrightarrow{\mathbf{d}}_q e^{i\mathbf{k}_q^T \mathbf{r}_x^B} \mathbf{P}_m^B(\mathbf{k}_q) = |\mathbf{0}|. \tag{89}$$

A common phase factor $\exp(i\mathbf{k}_q \mathbf{r}_x^B)$ can be eliminated from the expression. The result can be rewritten as

$$\overleftrightarrow{\mathbf{d}}_q \left[\sum_{j=1}^{N_s} e^{i\mathbf{k}_q^T(\mathbf{d}_S - \mathbf{r}_j)} \mathbf{p}_j + \sum_{w=1}^{N_B} \sum_{m=1}^{M} \nu_m \mathbf{P}_m^B(\mathbf{k}_q) \right] = |\mathbf{0}|. \tag{90}$$

Due to the projection character of the transverse projectors $\overleftrightarrow{\mathbf{d}}_q$,[8] we have to use projection again to filter out the independent parts. The efficient way to do this is by selecting a projection vector $\hat{\mathbf{t}}_q$ obeying

$$\hat{\mathbf{t}}_q^T \mathbf{k}_q = 0. \tag{91}$$

Suppose we have now an arbitrary vector $\mathbf{y}$, we apply $\mathbf{d}_q$ and project the result onto the $\hat{\mathbf{t}}_q$, then

$$\begin{aligned} \hat{\mathbf{t}}_q^T \overleftrightarrow{\mathbf{d}}_q \mathbf{y} &= \frac{i}{2\epsilon_0 |\mathbf{s}_1 \times \mathbf{s}_2| \kappa_q} \hat{\mathbf{t}}_q^T [k^2 \overleftrightarrow{\mathbf{1}} - \mathbf{k}_q \mathbf{k}_q^T] \mathbf{y} \\ &= \frac{i}{2\epsilon_0 |\mathbf{s}_1 \times \mathbf{s}_2| \kappa_q} [k^2 \hat{\mathbf{t}}_q^T \mathbf{y} - (\hat{\mathbf{t}}_q^T \mathbf{k}_q)(\mathbf{k}_q^T \mathbf{y})] \\ &= \frac{i}{2\epsilon_0 |\mathbf{s}_1 \times \mathbf{s}_2| \kappa_q} [k^2 \hat{\mathbf{t}}_q^T \mathbf{y}]. \end{aligned} \tag{92}$$

Using this result for the projection, we get for Eq. (90)

$$\sum_{j=1}^{N_S} e^{i\mathbf{k}_q^T(\mathbf{d}_S - \mathbf{r}_j)} \hat{\mathbf{t}}_q^T \mathbf{p}_j + \sum_{w=1}^{N_B} \sum_{m=1}^{M} \nu_m \hat{\mathbf{t}}_q^T \mathbf{P}_m^B(\mathbf{k}_q) = 0. \tag{93}$$

This result will add exactly one row to the double cell matrix. Addition of more columns in the surface part follows exactly the procedure as described before for Eq. (77). In practice we needed not one but two extra normal modes. This we achieved by selecting two different q's, the 10 and 02 channel to be precise (see the remark at the end of this section). For these channels we required the z-component of the corresponding $\hat{\mathbf{t}}_q$ to be zero:

$$t_{q,z} = 0. \tag{94}$$

Then condition (91) and normalization lead to

$$\begin{aligned} t_{q,x} k_{q,x} + t_{q,y} k_{q,y} &= 0, \\ t_{q,x}^2 + t_{q,y}^2 &= 1, \end{aligned} \tag{95}$$

which is enough to determine uniquely the $\hat{\mathbf{t}}_q$'s. We have to be keen in selecting our additional rows, since there can be more pairs q belonging to the same κ_q. A simple example are the (1,0) and (0,1) combination for a square lattice. Such pairs can result easily into two dependent rows and will cause the double cell interaction matrix to become singular.

D. Remote propagator

The (planar) remote propagator $\overleftrightarrow{\mathbf{f}}_R(\mathbf{R})$ links the microscopic response as given by the sources $\mathbf{p}_i$ and ν_m to the electric fields $\mathbf{E}_{\mathrm{Rem}}$ at a remote point $\mathbf{R}$. This propagator is exactly the same as for the local case and it suffices to repeat the results. The remote propagator itself is given for the case of reflection by the equation:

$$\begin{aligned} \mathbf{E}_{\mathrm{Rem}}(\mathbf{R}) &= \overleftrightarrow{\mathbf{f}}_R(\mathbf{R}) \mathbf{P}(\underline{\mathbf{k}}), \\ \overleftrightarrow{\mathbf{f}}_R(\mathbf{R}) &= \frac{ie^{i\underline{\mathbf{k}}^T \mathbf{R}}}{2\epsilon_0 |\mathbf{s}_1 \times \mathbf{s}_2||k_z|} [k^2 \mathbf{1} - \underline{\mathbf{k}}\underline{\mathbf{k}}^T], \end{aligned} \tag{96}$$

$$\mathbf{P}(\mathbf{k})=\sum_{j=1}^{N_S} e^{-i\mathbf{k}^T\mathbf{r}_j}\mathbf{p}_j+e^{-i\mathbf{k}^T\mathbf{d}_S}\sum_{m=1}^{M}\nu_m\mathbf{P}_m^B(\mathbf{k}),$$

where the cumulative normal mode dipole strength $\mathbf{P}_m^B(\mathbf{k})$ has been defined already in Eq. (72) (with $M=0$ this expression can be used for slabs). The remote fields can be used to generate all kinds of expressions used to describe the experimental observations. Only as an example, we give the expression for the reflection coefficient r_t, where t represents the polarization direction of the analyzer:

$$r_t=\frac{ik^2}{2\epsilon_0|\mathbf{s}_1\times\mathbf{s}_2||k_z|}\left[\frac{\hat{\underline{\mathbf{t}}}^T\mathbf{P}(\underline{\mathbf{k}})}{E_0}\right]. \tag{97}$$

The commonly used polarization directions s or p are just special cases of t.

VII. SUMMARY AND CONCLUSIONS

To describe a condensed matter system by means of discrete dipoles in the one-atom one-dipole assignment, requires the introduction of cells containing single atoms. When the electronic wave function cannot be confined to separate cells only (e.g., for semiconductors), cells will also influence each other directly quantum mechanically. This quantum induction requires the introduction of (quantum mechanical) nonlocal polarizabilities. A corresponding description of the system in terms of discrete dipoles and average electric fields is called discrete cellular method. The classical discrete dipole method in contrast uses local cellular polarizabilities and local (electric) fields. The solution of the electromagnetic part of the discrete cellular method has been given in this paper for finite, infinite, and semi-infinite systems. The final description for the crystalline semi-infinite case comes close to the double cell description derived by us before for the classical discrete dipole model. The nonlocal polarizabilities themselves cannot be obtained in a simple manner. They require a full quantum mechanical derivation and calculation. The complexity of that derivation is such that it will be published separately. An account of it can be found already in Ref. 11. What the precise influence of a discrete cellular description for a realistic system is, has been treated by us for the case of reflectance anisotropy of the GaAs (110) surface. The result is in much better agreement with experiment than has been possible by any other methods hitherto[10] for this system. A special point to be noted is that this result is obtained using the one-atom one-dipole assignment mentioned before. The current paper has shown that the inclusion of nonlocal polarizabilities is technically feasible and is only slightly more demanding than the equivalent discrete dipole calculation, as far as the electromagnetic part of the problem is concerned. The crucial difference between the classical discrete dipole method and current discrete cellular method is in the nonlocality. Discrete dipole methods account for only one kind of nonlocality: electric. Discrete cellular methods employ two kinds of nonlocality: electric and quantum mechanical.

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